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SELECTED ION FRAGMENTATION WITH A TANDEM QUADRUPOLE MASS SPECTR--ETC(U)
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SELECTED ION FRAGMENTATION WITH A TANDEM

QUADRUPOLE MASS SPECTROMETER.

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SELECTED ION FRAGMENTATION WITH A TANDEM
QUADRUPOLE MASS SPECTROMETER

ABSTRACT

A tandem quadrupole mass spectrometer is used to create ion species from a sample, separate one individual ion species, fragment it, and obtain the mass spectrum of the fragments. Practicability of the Selected Ion Fragmentation Tandem Quadrupole Mass Spectrometer (SIFT QMS) is experimentally demonstrated. Normally large ion losses due to scattering in the collision-induced dissociation (CID) process are eliminated by performing CID in a "RF-only" quadrupole. CID spectra with unit mass resolution are produced by the quadrupole mass filters. The CID spectrum of each component of a cyclohexane mixture containing three minor components is presented. Potential applications of SIFT QMS in mixture analysis and structure elucidation are discussed.

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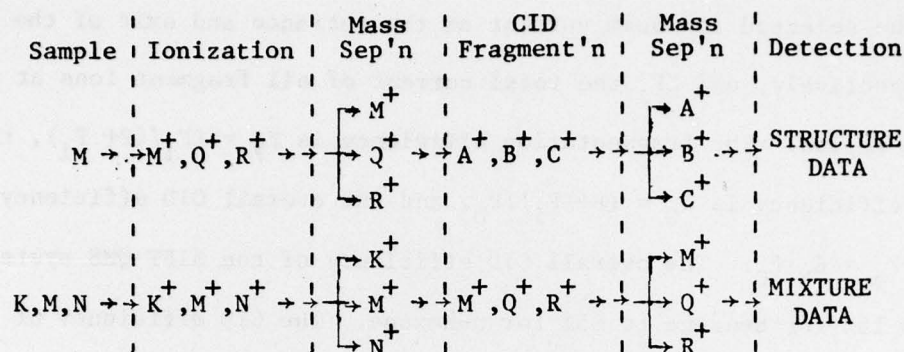
SELECTED ION FRAGMENTATION WITH A TANDEM
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Sir:

An added dimension of mass spectral information is provided by a tandem mass spectrometer when it is used to create ion species from a sample, select one individual ion species, fragment it, and obtain the mass spectrum of the fragments. Metastable ion peaks and collision-induced dissociation (CID) have been used to genetically relate daughter ions and their precursors.¹ Specialized "MIKES"² instruments have been developed to allow systematic acquisition of data on metastable and CID fragmentation spectra. A simple and very efficient system for obtaining mass spectra of the CID fragments of separated ions is the tandem quadrupole system described here. The system consists of, in series, a CI/EI ionization source, a quadrupole mass filter, an "RF-only" quadrupole CID region, a second quadrupole mass filter, and an electron multiplier.

The use of quadrupoles for mass separation provides higher transmission efficiency than magnetic sectors operated at the same resolution and mass range.³ Even more significant is the very high CID efficiency realized when CID occurs in an "RF-only" quadrupole. Unit mass resolution in the CID spectra is easily obtained with the tandem quadrupole system. Low sensitivity and low mass resolution of the CID spectra are reported for MIKES instruments.^{4,5,6} Because the tandem quadrupole mass spectrometer system is able to provide fragmentation spectra without loss of sensitivity or resolution, it is expected to be of particular value in mixture analysis (including the identification of impure compounds) and structure

elucidation applications. These applications are illustrated below.



Tandem quadrupole mass spectrometers have been developed for the study of ion-molecule reactions.^{8,9} A center "RF-only" quadrupole has been added for photodissociation studies^{10,11} and the investigation of long-lived metastable ions.¹² Prior to this study, however, all of the reported selected ion fragmentation work has been performed on reversed-sector MIKES instruments.^{1,4-6,13,14} Because the technique reported here uses two stages of mass separation rather than momentum and kinetic energy separations, the term MIKES does not apply. We therefore suggest the generally applicable name, "Selected Ion Fragmentation Tandem Mass Spectrometry", or SIFT MS, and in the tandem quadrupole implementation described here, SIFT QMS.

Preliminary SIFT QMS experiments have been performed on a tandem quadrupole mass spectrometer¹¹ in the laboratory of J.D. Morrison at LaTrobe University, Bundoora, Victoria, Australia. The EI source sensitivity was 3×10^{-5} A/torr of cyclohexane (1 ion/ 10^5 molecules). Transmission through the ion optics into the first quadrupole was 30%. In RF-only mode, quadrupole transmission was 30%. In mass filter mode, transmission dropped to 2.5%. Neglecting CID, this gives an overall sensitivity of 1.5×10^{-9} A/torr of cyclohexane (5 ions detected/ 10^{10} sample molecules).

The efficiency of the CID process is determined by two factors, the fragmentation efficiency and the collection efficiency. We can let P_0 and P symbolize the selected ion beam current at the entrance and exit of the CID region, respectively, and ΣF_i the total current of all fragment ions at the exit of the region. The fragmentation efficiency is $E_F = \Sigma F_i / (P + F_i)$, the collection efficiency is $E_C = (P + \Sigma F_i) / P_0$, and the overall CID efficiency is $E_{CID} = \Sigma F_i / P_0 = E_F \cdot E_C$. The overall CID efficiency of the SIFT QMS system ranges from 15% for benzene to 65% for n-hexane. The CID efficiency of a MIKES instrument has recently been reported as less than 10%.¹ The collection efficiency in the SIFT QMS system is nearly 100%; there is virtually no scattering loss in the CID process, even at 2×10^{-4} torr CID pressure (the maximum obtainable with this instrument). In SIFT QMS, CID occurs in a strong-focusing quadrupole field; the field-free drift region used for CID in MIKES instruments produces scattering losses of 90% (collection efficiency of 10%) at similar CID pressures.¹³

The scattering losses in the MIKES CID chamber increase as the mass of the collision gas increases. This has led to a preference for Hydrogen or Helium as the collision gas.^{6,13} Because the collection efficiency is 100% in the quadrupole CID region, heavier collision gases can be used to increase the fragmentation efficiency. Argon shows CID efficiencies three to four times higher than Hydrogen in SIFT QMS.

To demonstrate the mixture analysis capabilities of the SIFT QMS system, a mixture of cyclohexane and three minor components (benzene, n-hexane, and cyclohexanone, each present a 5% of the mixture), was analyzed. The CID spectrum of the parent ion of each of the four components was obtained; that for cyclohexanone is shown in Figure 1. The CID spectra of all the mixture

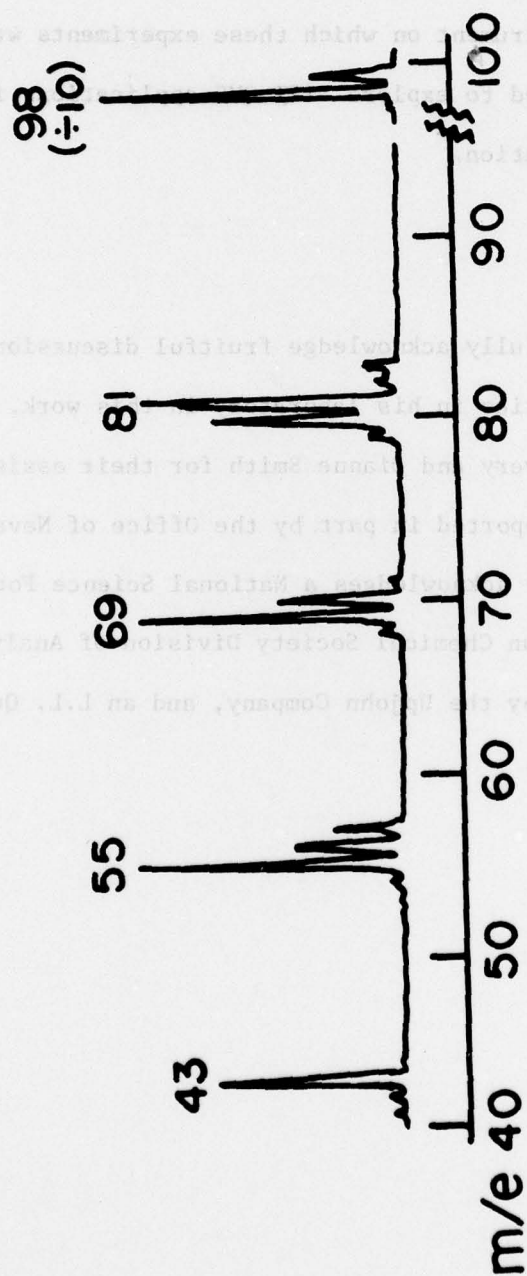


FIGURE 1. CID Spectrum of the Parent Ion (m/e 98) of Cyclohexanone Present as 5% of a Mixture

components are reproducible, show good agreement with the CID spectra of the pure compounds, and resemble the 14-16 eV EI spectra of the pure compounds.

A tandem quadrupole system for SIFT QMS is currently under construction in this laboratory. It will have a dual CI/EI source, more efficient quadrupoles with a larger mass range, and be able to tolerate higher CID pressure than the instrument on which these experiments were performed. This instrument will be used to explore SIFT QMS applications in mixture analysis and structural elucidation.

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